Indian J. Phys. **72A** (2), 133–139 (1998)

IJP A
- an international journal

Evaluation of the trapping parameters of TL peaks of multi activated SrS phosphors

W Shambhunath Singh[a], S Joychandra Singh[b], N C Deb[c], Manabesh Bhattacharya[d], S Dorendrajit Singh[e] and P S Mazumdar[c, f]

[a]Department of Physics, Manipur College, Imphal, Singjamei-795 008, Manipur, India

[b]Ballistics Division, Manipur State Police Forensic Laboratory, Pangei Yangdong-795 114, Manipur, India

[c]Center for Theoretical Studies of Physical Sciences, Clark Atlanta University, Atlanta, Georgia 30314, USA

[d]Department of Theoretical Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

[e]Department of Physics, School of Science, Manipur University, Chanchipur, Imphal-795 003, Manipur, India

[f]Present Address :

Department of Physics, Acharya Prafulla Chandra College, Sajirhat, New Barrackpore-743 276, North 24 Parganas, West Bengal, India

Received 2 May 1997, accepted 4 February 1998

Abstract : In the present paper we suggest a relation connecting the symmetry factor (μ_g) and order of kinetics (b) so that one can directly determine b once μ_g is known. We also extend the work of Gartia *et al* for a wider range of b values ($0.4 \leq b \leq 4$). As rough check of the theoretical methods we determine the trapping parameters namely activation energy, order of kinetics and frequency factor of thermoluminescence (TL) peaks of multi activated SrS phosphors reported by Rao *et al*. The present values of activation energy differ appreciably from those of Rao *et al* obtained by using some crude methods

Keywords : Thermoluminescence, order of kinetics, activation energy

PACS No. : 78.60.Kn

1. Introduction

Thermoluminescence is the light emitted from an insulator or a semiconductor as a result of heating after exposing it to some ionising radiation. TL is an indispensable tool for exhaustive study of the nature of thermal stability and concentrations of both electron and hole trapping centres in luminescent materials. It has found important applications in dating

and dosimetry [1]. The shape, position and intensity of a TL peak are related to various trapping parameters namely order of kinetics (b), frequency factor (s) and activation energy (E). The various methods for determination of trapping parameters have been reviewed by Chen and Kirsh [1], McKeever [2], Kirsh [3] and more recently by Gartia *et al* [4].

In a recent work Rao *et al* [5] have presented TL data of multi activated SrS phosphors. They evaluated activation energy of TL peaks recorded by them. But in spite of recent developments in the analysis of trapping parameters of TL peaks they use outdated and crude methods of Urbach [6] and Randall and Wilkins [7]. For example, it has been shown by Christodoulides [8] that Urbach method was meant as a very rough guide and as such it is of limited accuracy. It gives an activation energy value which may be wrong by upto a factor of two either way. They [5] also assume mono molecular kinetics ($b = 1$) and a frequency factor $s = 10^9$ sec^{-1} without any justification. It is well known [1,2] that a TL peak can be characterised by a parameter called the symmetry factor μ_g defined by

$$\mu_g = \frac{T_m - T_1}{T_2 - T_1} \tag{1}$$

where T_m is the peak temperature, T_1, T_2 are the temperatures at which the intensity is equal to half of the maximum intensity on either side of T_m ($T_2 > T_1$). It is well known [1–4] that μ_g ~0.42 for $b = 1$ and μ_g ~0.52 for $b = 2$. In Table 1, we calculate μ_g for TL peaks recorded

Table 1. Trapping parameters E, s and b of TL peaks of multi activated SrS phosphors reported by Rao *et al* [5] by using the present method Samples of series A contain Gd in fixed amount and concentrations of Cu and Mn are varying Similarly in series B, concentration of Mn is fixed while those of Gd and Cu are varying. In series C, Cu concentration is fixed and those of Mn and Gd are varied

No	Sample name	T_m (°K)	μ_g	b	E_τ (eV)	E_δ (eV)	E_ω (eV)	s (s^{-1})
16	SrS : Mn	367	0 467	1 48	0 500	0 548	0 524	$1\ 22 \times 10^6$
22	SrS Cu	359	0.400	0 95	0.375	0 426	0 396	$2\ 61 \times 10^4$
24	SrS Cu, Mn	343	0 552	2.42	0.626	0.624	0 625	$1\ 53 \times 10^8$
25	SrS . Gd	345	0 333	0.51	0 410	0.411	0.411	$7\ 64 \times 10^4$
A1	SrS : Gd, (Cu, Mn)	363	0 487	1 67	0.386	0 432	0 409	2.87×10^4
A2	do	343	0.585	3 05	0 804	0.777	0.788	4.94×10^{10}
A3	do	350	0 500	1.79	0.579	0 607	0.594	$3\ 29 \times 10^7$
A4	do	357	0.510	1.90	0.701	0 718	0 710	$1\ 15 \times 10^9$
A5	do	358	0.491	1 70	0.574	0 609	0 592	1.95×10^7
A	do	360	0 480	1.60	0 622	0.660	0.641	$9\ 23 \times 10^7$
A6	do	356	0.421	1 11	0 421	0 474	0.445	1.54×10^5
A7	do	375	0 433	1.20	0 464	0 520	0 490	2.86×10^5
B2	SrS.: Mn, (Cu, Gd)	344	0.477	1.57	0.646	0 681	0 663	5.84×10^8
B5	do	360	0.420	1 10	0.500	0.552	0 523	1.88×10^6
C′	SrS : Cu, (Mn, Gd)	360	0.480	1.60	0.622	0.660	0.641	9.23×10^7
C3	do	355	0.426	1 14	0 531	0.582	0.554	7.03×10^6
C5	do	362	0.378	0.80	0.491	0.530	0.507	1.03×10^6
C7	do	373	0.435	1.22	0.445	0.501	0 471	1.66×10^5

by Rao *et al* [5]. It is seen from Table 1 that μ_g values range from 0.333 to 0.585. So it is not appropriate to make the mono molecular assumption as above by Rao *et al* [5]. In the present paper, we analyse the TL peaks recorded by Rao *et al* [5] by using the peak shape method of Gartia *et al* [9].

We also suggest a method for the estimation of the order of kinetics (b) from μ_g which is more objective than the conventional method of Chen [10] and extend the work of Gartia *et al* [9] for a wider range of b values namely ($0.4 \leq b \leq 4$).

2. Theory

The equation for the first order ($b = 1$) and general order ($b \neq 1$) TL peaks can be written as [8,9,11,12]

$$I/I_m = \exp\left(u_m - u + F(u, u_m)\right), \quad (b = 1) \tag{2}$$

and

$$I/I_m = \exp(u_m - u)\left\{1 - [(b-1)/b]\, F(u, u_m)\right\}^{-b/(b-1)}, \quad (b \neq 1) \tag{3}$$

with

$$F(u, u_m) = u_m^2 \exp(u_m)\left\{E_2(u_m)/u_m - E_2(u)/u\right\}, \tag{4}$$

where I and I_m are respectively the TL intensities at any temperature T and peak temperature T_m. $E_2(u)$ is the second exponential integral [13]. The variable u is defined as $u = E/kT$, similarly $u_m = E/kT_m$.

The eqs. (2) and (3) can be solved by an iterative technique [8,11,12] to determine the half intensity temperatures T_1 and T_2 for which $I/I_m = 1/2$. Knowing half intensity temperatures T_1 and T_2, symmetry factor μ_g can be calculated from eq. (1). It has been observed by Gartia *et al* [9,11] that μ_g is a function of u_m and b but the dependence of μ_g on b is much more stronger than that on u_m. This point has also been observed by Chen [10] who instead of considering the dependence of μ_g on u_m considered its dependence on the activation energy E and frequency factor s separately. Chen [10] has also presented a graphical method for the determination of the order of kinetics (b) from symmetry factor μ_g. Moreover, both Gartia *et al* [11] and Chen [10] considered values of b between 0.7 and 2.5. But Kirsh [3] considered an order of kinetics range from 0.5 to 3.0. In the present paper, we consider the range of b values between 0.4 and 4.0. For most of the observed TL peaks u_m ranges from 20 to 40. As a result, we have calculated the average μ_g for $20 \leq u_m \leq 40$ for each value of b between 0.4 and 4.0. Finally, the average μ_g has been expressed as a quadratic function of b ($0.4 \leq b \leq 4.0$) using the technique of non linear regression [14] as

$$\mu_g = 0.2453420 + 0.1858256\, b - 0.0244183\, b^2. \tag{5}$$

In Figure 1, we exhibit the quadratic plot of μ_g against b. Knowing μ_g, b can be determined from eq. (5). For a particular μ_g, eq. (5) being quadratic in b will give two values of b. One has to take the value of b which lies between 0.4 and 4.0. We feel that the present method

for the determination of the order of kinetics b is more objective than the graphical method of Chen [10]. We also see that for $b = 1$, $\mu_g \sim 0.42$ and for $b = 2$, $\mu_g \sim 0.52$ as expected.

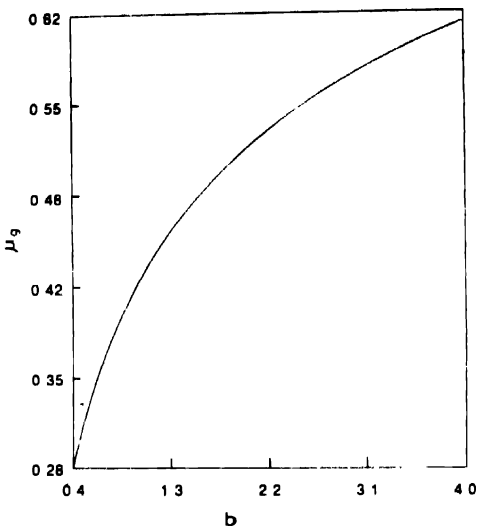

Figure 1. A plot of average μ_g as a function of b illustrating their quadratic relationship for $0.4 \leq b \leq 4.0$

Again following Gartia *et al* [9], it has been found that a good linear correlation exists between the following pairs of variables :

$$\left(u_m, u_1/(u_1 - u_m)\right)$$

$$\left(u_m, u_2/(u_m - u_2)\right)$$

and $$\left(u_m, u_1 u_2/\left[u_m(u_1 - u_2)\right]\right)$$

with $u_1 = E/kT_1$ and $u_2 = E/kT_2$ so that one can write

$$u_m = C_\tau u_1/(u_1 - u_m) + D_\tau, \tag{6}$$

$$u_m = C_\delta u_2/(u_m - u_2) + D_\delta, \tag{7}$$

$$u_m = C_\omega u_1 u_2/u_m(u_1 - u_2) + D_\omega, \tag{8}$$

where the coefficients C_j and D_j ($j = \tau, \delta, \omega$) occurring in eqs. (6–8) are dependent on the order of kinetics (b). The eqs. (6–8) can be recast in the following forms

$$E_\tau = C_\tau kT_m^2/\tau + D_\tau kT_m, \tag{9}$$

$$E_\delta = C_\delta kT_m^2/\delta + D_\delta kT_m, \tag{10}$$

$$E_\omega = C_\omega kT_m^2/\omega + D_\omega kT_m, \tag{11}$$

where $\tau = T_m - T_1$, $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$.

By using the method of least square regression [14] each of the coefficients C_j and D_j can be expressed as a quadratic function of b

$$C_j = C_{0j} + C_{1j}b + C_{2j}b^2; \tag{12}$$

$$D_j = D_{0j} + D_{1j}b + D_{2j}b^2. \tag{13}$$

The coefficients C_{kj} and D_{kj} ($k = 0$–2) are presented in Table 2.

Table 2. Coefficients C_{kj} and D_{kj} ($k = 0-2, j = \tau, \delta, \omega$) occurring in eqs (12–13)

j	C_{0j}	C_{1j}	C_{2j}	D_{0j}	D_{1j}	D_{2j}
τ	0.6967	0.3869	–0.0390	–0.7419	–1.1511	0.0758
δ	0.1593	0.6454	–0.0336	0.2080	–0.4920	–0.0707
ω	0.8561	1.0312	–0.0725	–0.5221	–0.6187	–0.0250

The present coefficients are somewhat different from those of Gartia *et al* [9] because in the present work, a wider range of b values have been used. Now knowing b for a particular μ_g from eq. (5), one can evaluate E_τ, E_δ and E_ω from eqs. (9–11). Once the activation energy and the order of kinetics are known, one can determine the frequency factor s from the relations (1–4).

$$s = \beta\left[E/(kT_m^2)\right]\exp(u_m), \quad (b = 1) \tag{14}$$

$$s = \beta\Big/\left\{b\left(kT_m^2/E\right)\exp(-u_m) - (b-1)\int_{T_0}^{T_m}\exp\left[-E/(kT)\right]dT\right\}, \quad (b \neq 1) \tag{15}$$

where β is the heating rate, T_0 is the initial temperature. The integral $\int_{T_0}^{T_m}\exp[-E/(kT)]dT$ appearing in eq. (15) cannot be solved analytically and therefore has been developed as

$$\int_{T_0}^{T_m}\exp\left[-E/(kT)\right]dT = \int_{0}^{T_m}\exp\left[-E/(kT)\right]dT - \int_{0}^{T_0}\exp\left[-E/(kT)\right]dT,$$

$$= (E/k)\left\{\int_{u_m}^{\infty}\left[\exp(-u)/u^2\right]du - \int_{u_0}^{\infty}\left[\exp(-u)/u^2\right]du\right\},$$

$$= (E/k)\left\{E_2(u_m) - E_2(u_0)\right\}, \tag{16}$$

where $u_m = E/kT_m$ and $u_0 = E/kT_0$. $E_2(u)$ have been calculated by following the technique outlined by Mazumdar *et al* [12] and Gartia *et al* [11].

3. Results and discussion

The suitability of the present peak shape method has been judged by applying it to a number numerically computed TL peaks. It is seen from Table 3 that there is a good

agreement between the input and the computed values of trapping parameters. In Table 1, the trapping parameters of TL peaks of multi activated phosphors recorded by Rao *et al* [5] have been evaluated. As expected the values of activation energies are very much different from those obtained by Rao *et al* [5]. The order of kinetics is not one as assumed by them and the frequency factor s calculated using the average of E_τ, E_δ and E_ω, is also widely different from the value 10^9 assumed by them.

Table 3. Trapping parameters of some computer generated TL peaks by using the present method.

Input values of			Calculated values of						
E (eV)	s (s^{-1})	b	T_m (°K)	μ_g	b	E_τ (eV)	E_δ (eV)	E_ω (eV)	s (s^{-1})
1.6	10^{13}	0.7	555.6	0.364	0.70	1.600	1.600	1.600	1.04×10^{13}
1.6	10^{13}	1.0	555.3	0.417	1.07	1.610	1.676	1.639	2.43×10^{13}
1.6	10^{13}	1.5	554.9	0.476	1.56	1.603	1.635	1.619	1.50×10^{13}
1.6	10^{13}	2.0	554.5	0.517	1.97	1.593	1.578	1.586	7.35×10^{12}

4. Conclusion

In the present paper, we extend the peak shape method of Gartia *et al* [9] and suggest a formula for the direct computation of the order of kinetics from the observed value of the symmetry factor. By applying the present method to TL peaks of multi activated SrS phosphors reported by Rao *et al* [5], it is found that the trapping parameters computed by them using some crude methods are widely different from that calculated by using the present method.

Acknowledgments

The authors thank Professor R K Gartia for fruitful discussions. One of the authors (MB) would like to thank the Council of Scientific and Industrial Research, India for providing partial financial support. The authors are grateful to the referee for his critical comments on the paper.

References

[1] R Chen and Y Kirsh *Analysis of Thermally Stimulated Processes* (Oxford : Pergamon) Chap 6 (1981)

[2] McKeever *SWS Thermoluminescence of Solids* (Cambridge : Cambridge University Press) (1985)

[3] Y Kirsh *Phys Stat Sol (a)* **129** 15 (1992)

[4] R K Gartia, S D Singh, P S Mazumdar and N C Deb *Indian J. Phys.* **71A** 95 (1997)

[5] A P Rao, V G Machwe and A S Mehta *Indian J. Pure Appl. Phys.* **34** 937 (1996)

[6] F Urbach *Weiner Ber. IIa* **139** 363 (1930)

[7] J T Randall and M H F Wilkins *Proc. Roy. Soc.* **A184** 364 (1945)

[8] C Christodoulides *J. Phys.* **D18** 1501 (1985)

[9] R K Gartia, S J Singh and P S Mazumdar *Phys Stat. Sol.* **114** 407 (1989)

[10] R Chen *J. Electrochem. Soc.* **116** 1254 (1969)

[11] R K Gartia, S J Singh and P S Mazumdar *Phys. Stat. Sol. (a)* **106** 291 (1988)

[12] P S Mazumdar, S J Singh and R K Gartia *J Phys.* **D21** 815 (1988)

[13] M Abramowitz and I A Stegan *Hand Book of Mathematical Functions* (Dover : New York) Chap 5 (1965)

[14] E J Dudewicz and S N Mishra *Modern Mathematical Statistics* (New York : Wiley) Chap 14 (1988)